Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Alternative

Diana Facchini
Integran Technologies Inc.

Ruben A. Prado
NAVAIR Jacksonville

ASETS Defense Workshop
Sustainable Surface Engineering for Aerospace & Defense
September 2, 2009

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
02 SEP 2009		**00-00-2009 to 00-00-2009**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Electrodeposition of Nanocrystalline Co‐P Coatings as a Hard Chrome Alternative	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Integran Technologies Inc.,1725 Washington Road, Suite 305,Pittsburgh,PA,15241-1209**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
ASETSDefense 2009: Sustainable Surface Engineering for Aerospace and Defense Workshop, August 31 - September 3, 2009, Westminster, CO. Sponsored by SERDP/ESTCP.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**29**	

Hard Chrome Plating
(Why do we use it?)

- **Why Chrome plating?**

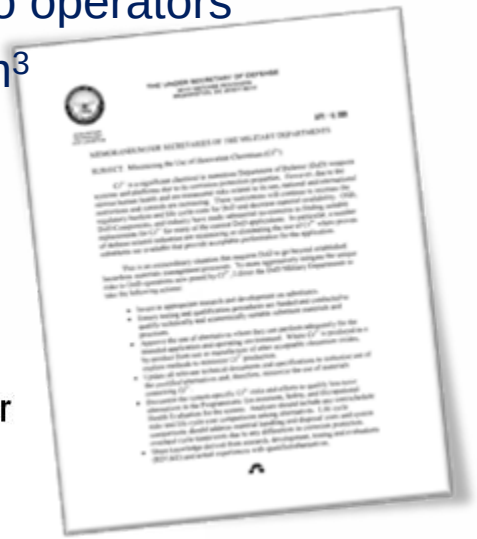
  Engineering hard chrome (EHC) coatings are used extensively in both industry and military applications due to their excellent performance characteristics.

  - Wear
  - Corrosion Resistance
  - Restore Dimensions

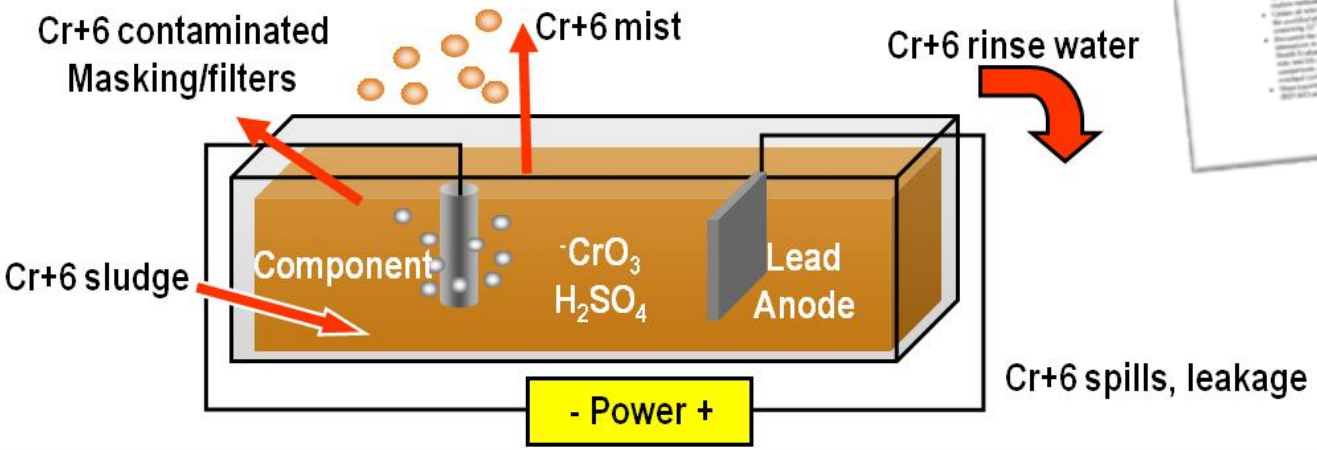
- **Where is Chrome Plating Used?**
  - OEM and rebuild/repair
  - Helicopter dynamic components
  - Hydraulic actuators
  - Propeller hubs
  - Gas turbine engines
  - Landing Gear

Hard Chrome Plating
(The Problem)

- **Hard Chrome Plating Environmental & Health Hazards**
  - Hard chrome plating utilizes chromium in the hexavalent state (Cr^{6+})
  - Cr^{6+} is a known carcinogen and poses a health risk to operators
  - OSHA lowered the Cr^{6+} PEL from 52 µg/m^3 to 5 µg/m^3



- **8 Apr 09, Memorandum, DoD Directive**
  - Hexavalent Chromium Management Policy



Current Alternatives to EHC

- **Line-of-Sight Application (LOS)**
  - Thermal spray
  - HVOF (High Velocity Oxygen Fuel) Coatings

- **Non line-of-sight applications (NLOS)**
  - Ni based electroless (Ni-P and Ni-B) coatings
  - Ni based electrolytic (Ni-W, Ni-Co, Ni-Mo, etc.) coatings
  - Ni listed among EPA's 17 most toxic heavy metals

- **Proposed Solution:**

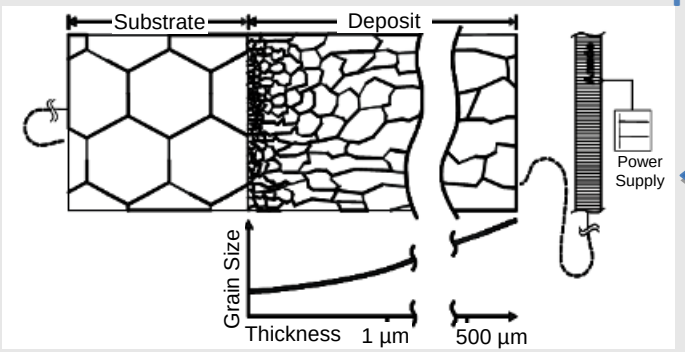
  Nanocrystalline Cobalt Phosphorus (nCoP) electroplating as an alternative to EHC for both LOS and NLOS applications for Depot rework. Co PEL is 20 µg/m^3*

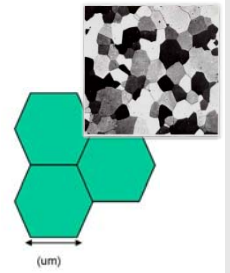
**MERIT policies on Emerging Contaminants per DODI 4715.18 being monitored. Phase I Impact Assessments are planned for manganese and cobalt. Report pending.*

Electrodeposited Nanocrystalline Materials

- **Pulsed Current Waveform Engineering**
  - Favors nucleation of new grains over growth
  - Results in an ultra-fine grain structure
  - Uniform throughout thickness
  - Reduces average Grain Size
- **Leads to unique properties**
  - ↑ Yield Strength, wear, ultimate tensile strength
  - ↓ Coefficient of friction

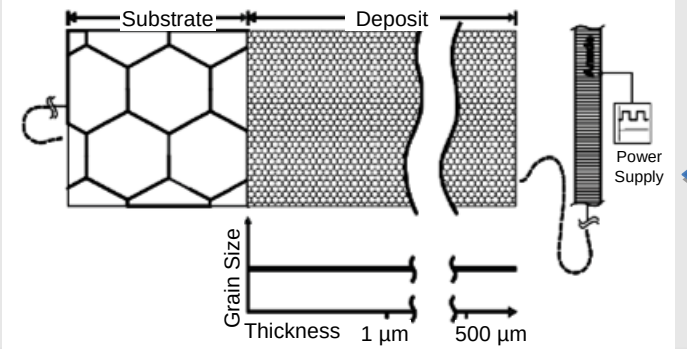
Conventional Electrodeposits

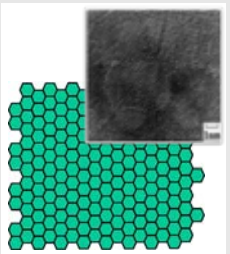




Polycrystalline (10-100 µm)

Nanocrystalline Electrodeposits





Nanocrystalline (< 100 nm)

nCoP (aka Nanovate™ CR) Electrodeposition Process

- **High deposition rate**
  - At 8X faster than Chrome plating / increase throughput
- **High current efficiency**
  - Reduced power consumption (90% reduction)
- **Drop-in technology**
  - Compatible with current EHC plating infrastructure
  - Can be applied to both LOS and NLOS surfaces

	nCoP	EHC
Deposition Method	Electrodeposition (Pulse)	Electrodeposition (DC)
Part Geometries	LOS and NLOS	LOS and NLOS
Efficiency	85-95%	15-35%
Deposition Rate	0.002”-0.008” /hr	0.0005”-0.001” /hr
Emission Analysis	Below OSHA limits	Cr+6

nCoP Properties

nCoP

Cross section of nCoP deposit.

No pits, cracks or pores.

EHC

Cross section of EHC deposit.

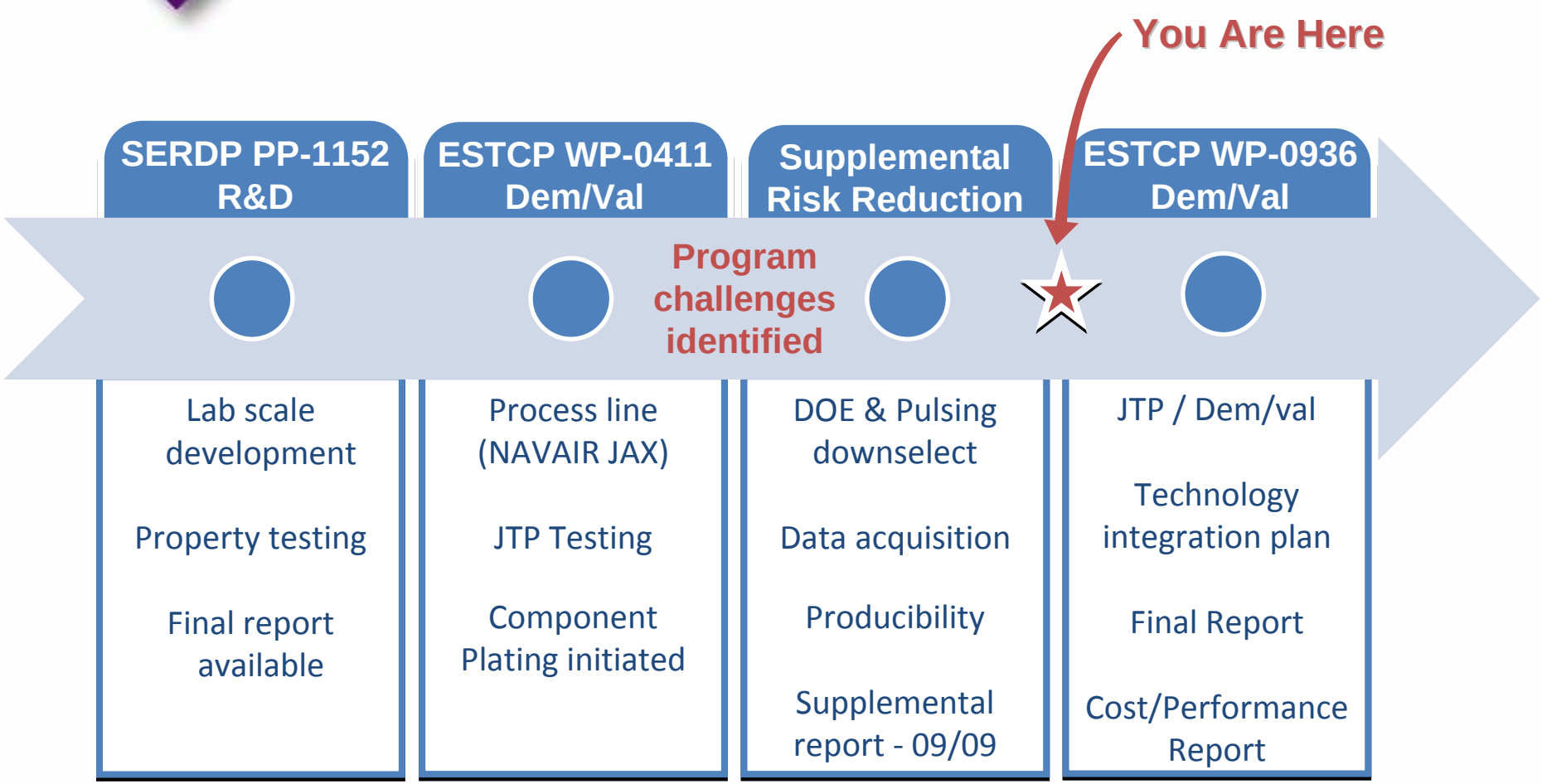
Microcracking observed.

nCoP Properties

		nCo-P	EHC
Appearance		Pit, Pore, Crack -free	Microcracked
Ductility		2-7%	<1%
Hardness	*As-Deposited*	530-600 VHN	Min. 600 VHN
	Heat Treated	up to 680 VHN	-
Adhesive Wear (Pin-on-disk)	*Wear volume loss*	6-7 x 10^{-6} mm^3/Nm	9-11 x 10^{-6} mm^3/Nm
	Coefficient of friction	0.4-0.5	0.7
	Pin Wear	Mild	Severe
Corrosion	*Salt Spray ASTM B117*	† Protection Rating 8 (1000 h) @ 0.002”	† Protection Rating 2 (1000 h) @ 0.004”
Hydrogen Embrittlement	ASTM F519	Pass with bake	Pass with bake

†*ASTM B537 Rating*

Progress


You Are Here
SERDP PP-1152 R&D
ESTCP WP-0411 Dem/Val
Supplemental Risk Reduction
ESTCP WP-0936 Dem/Val
Program challenges identified
Lab scale development
Property testing
Final report available
Process line (NAVAIR JAX)
JTP Testing
Component Plating initiated
DOE & Pulsing downselect
Data acquisition
Producibility
Supplemental report - 09/09
JTP / Dem/val
Technology integration plan
Final Report
Cost/Performance Report

Plating Parameter Downselect

SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

- **Design of Experiments approach**
  - 2^3 full factorial design

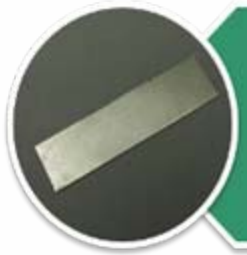
Current Density	Frequency*	Duty Cycle**
1	1	1
1	1	-1
1	-1	1
1	-1	-1
-1	1	1
-1	1	-1
-1	-1	1
-1	-1	-1
0	0	0

* $f = 1/(t_{on}+t_{off})$

** $t_{on}/(t_{on}+t_{off})x100$

Hydrogen Embrittlement Bar
Hydrogen Embrittlement
Appearance
Adhesion

Stress Strip
Internal Stress



Flat Plate

Adhesion	Composition
Appearance	Hardness
Efficiency	Microstructure
Thickness	Plating rate

Plating Parameter Downselect

SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

- Hydrogen Embritttlement testing (ASTM F519)
  - No post-plating hydrogen embrittlement relief bake (all pass with bake)

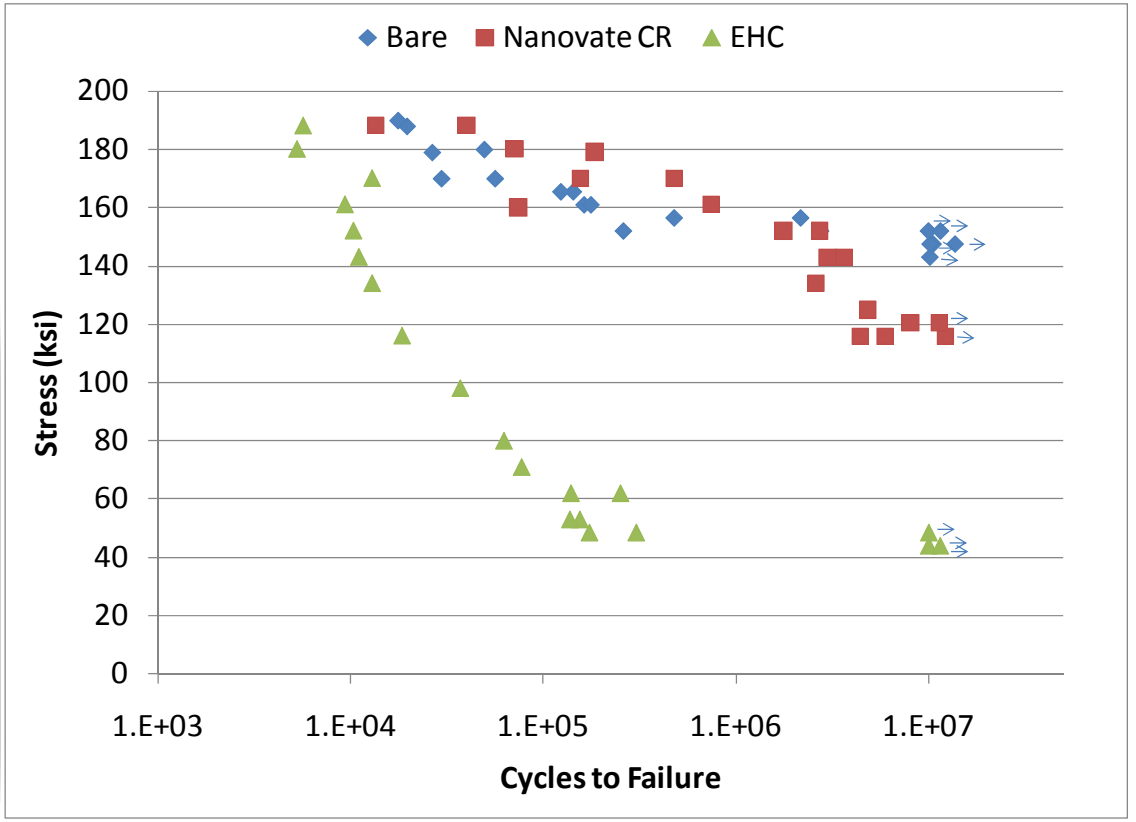
- No statistically significant effect of plating conditions

Current Density	Frequency	Duty Cycle	Time to failure, h			
			Bar 1	Bar 2	Bar 3	Bar 4
1	1	1	40	121	193	193.1
1	1	-1	> 200	> 200	> 200	> 200
1	-1	1	49	57	58	> 200
1	-1	-1	> 200	> 200	> 200	> 200
-1	1	1	136	193	200	> 200
-1	1	-1	80	80	121	193
-1	-1	1	> 200	> 200	> 200	> 200
-1	-1	-1	> 200	> 200	> 200	> 200
0	0	0	80	123	137	> 200

Data Acquisition
(Rotating Beam Fatigue)

SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

- **Testing with downselected plating conditions**
- Hourglass geometry
- 4340 substrate
  - 260-280 ksi
  - No shot peen



**Unofficial results obtained from supplemental testing using optimized parameters*

Data Acquisition
(Summary)

SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

- **Testing with downselected plating conditions**

Property	Test	Result
Microstructure	X-ray diffraction	Nanocrystalline
Stress	Stress strips	10-15 ksi (tensile)
Adhesion	Bend test	Pass
Porosity	Microscopy	Fully dense
Hydrogen embrittlement	ASTM F519	Pass
Corrosion	ASTM B117 salt spray 165h	Pass
Hardness	Vicker's Microhardness	560 VHN
Abrasive Wear	Taber	17 mg/1000 cycles
Fatigue	Rotating beam	Comparable to bare Credit vs. EHC

Optimized Pulse Conditions Established

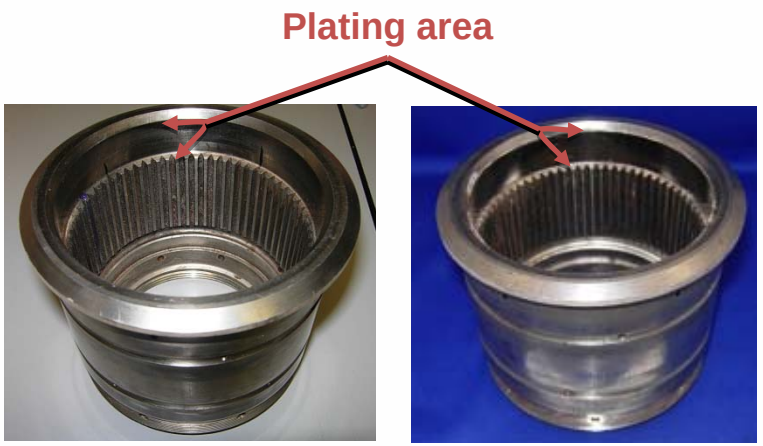
Panel plated using downselected parameters

Producibility

SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

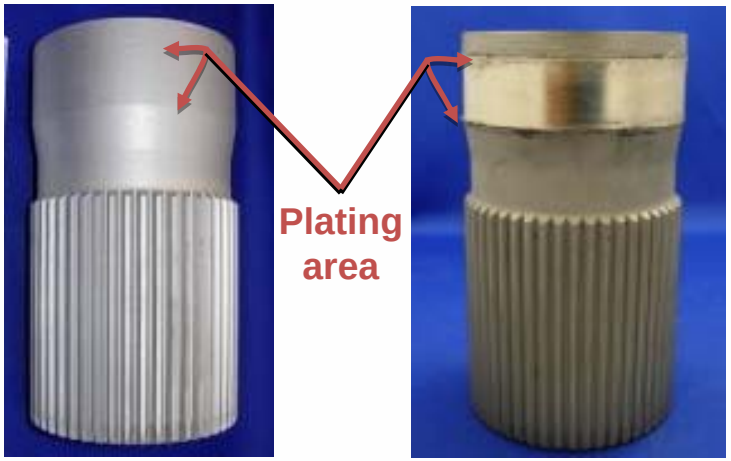
- **Producibility with downselected plating conditions**
- nCoP applied to internal and outer diameter sections

Internal Diameter Plating J52 Coupling



As-received nCoP-plated

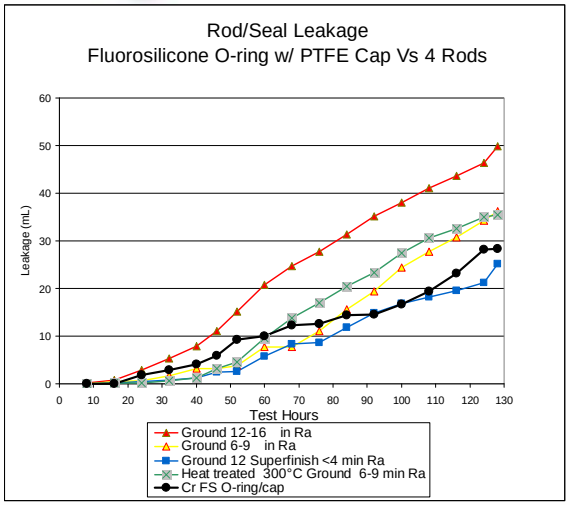
Outer Diameter Plating J52 Shaft (section)

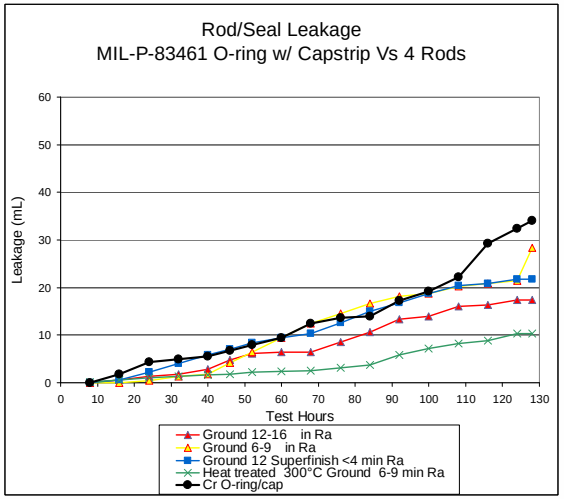


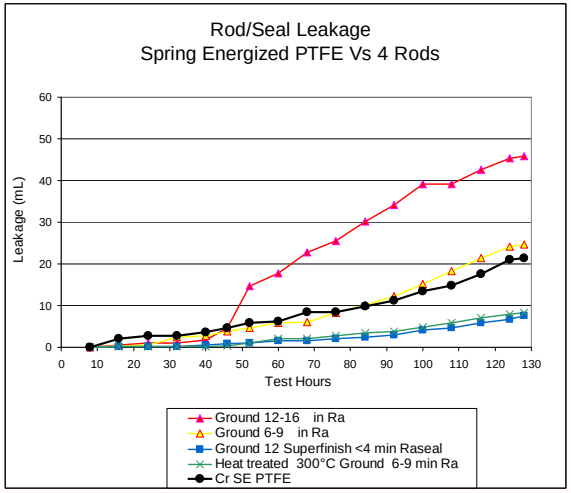
As-received nCoP-plated

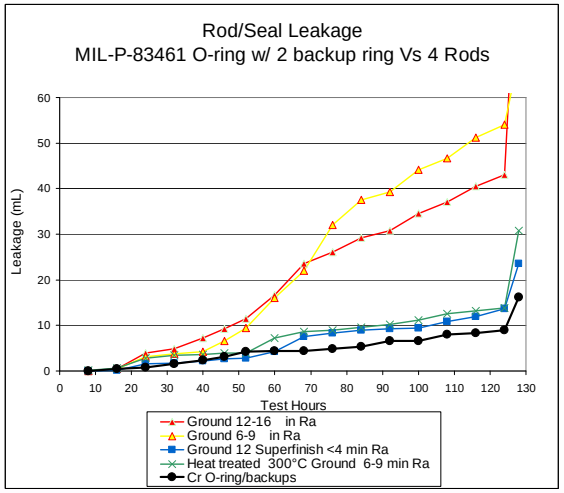
Rod-Seal Wear
(Leakage, Various O-rings)

SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936









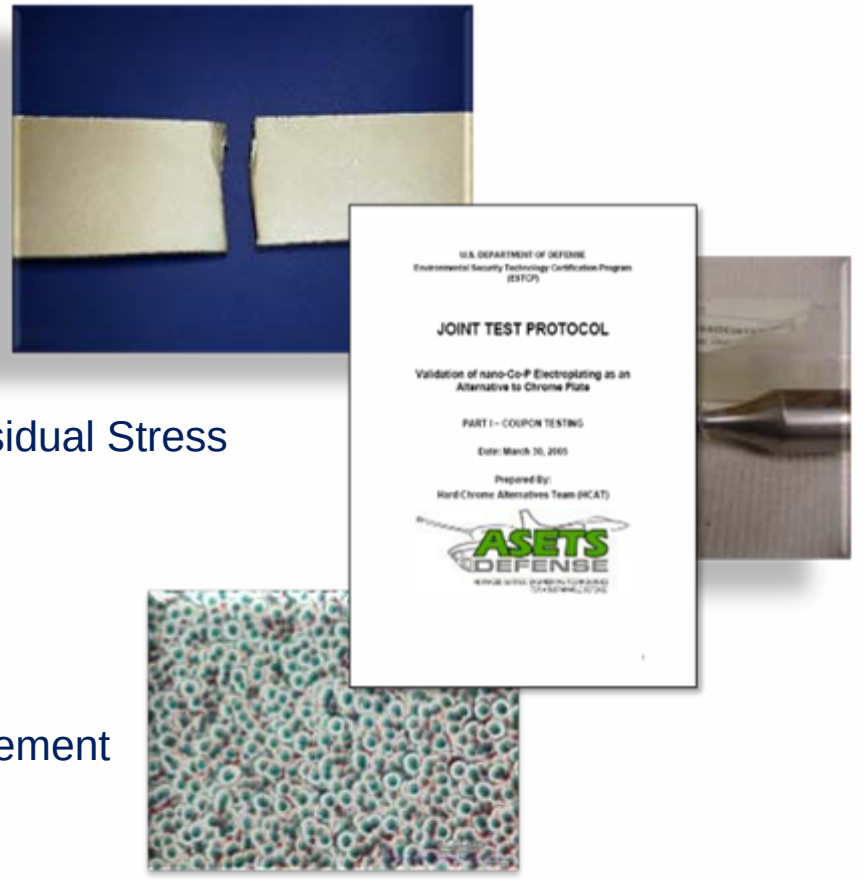
Black lines hard chrome from prior HCAT work

- Different test run
- nCoP roughly comparable with hard chrome
- Ground surfaces higher leakage

Future Work

SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

- **Demonstration Plan and Joint Test Protocol will be developed by team members**
- Stakeholders:
  - NAVAIR (JAX, PAX, CP, Lakehurst)
  - NAVSEA
  - Integran
  - OEM
- Key JTP Performance Criteria:
  - Coating Properties:
    - Microstructure, % P, Hardness, Residual Stress
  - Coating Performance:
    - Corrosion testing
    - Fatigue testing
    - Wear
    - Hydrogen & Environmental Embrittlement
  - Chemical compatibility tests
  - Rig Testing (where applicable)



Demonstration Site

SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

- **NAVAIR JAX Depot**
  nCoP Dem/Val Process Line
  - 250 gallon nCoP Tank (2.5'x4'x4')
  - 370 gallon Activation Tank (3'x3'x6')
  - Pulse Power Supply (1500A Peak Current)
  - Remote Controller (Touch Screen)

nCoP Dem/Val tank

Power Supply

Remote Controller

Acid/Fluoride Activation tank

Proposed Demo Components

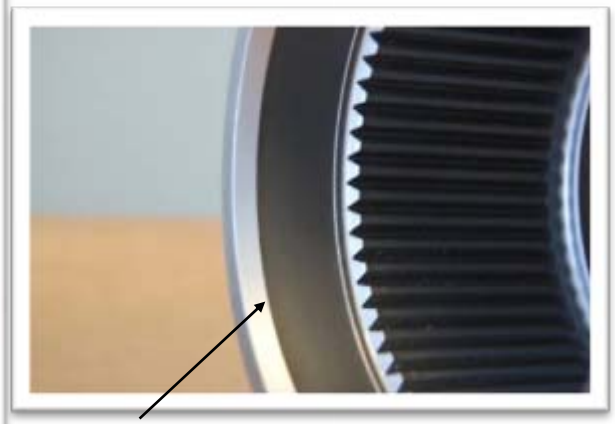
SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

NAVAIR JAX for Air Vehicle Components

- **J-52 Coupling, Turbine Shaft Actuating Cylinder (for production capability)**

J-52 Coupling, Turbine Shaft
Material: 4340 Steel (AMS 6415)

Demo part shown in rack assembly with titanium basket anode in place



ID area to receive plating

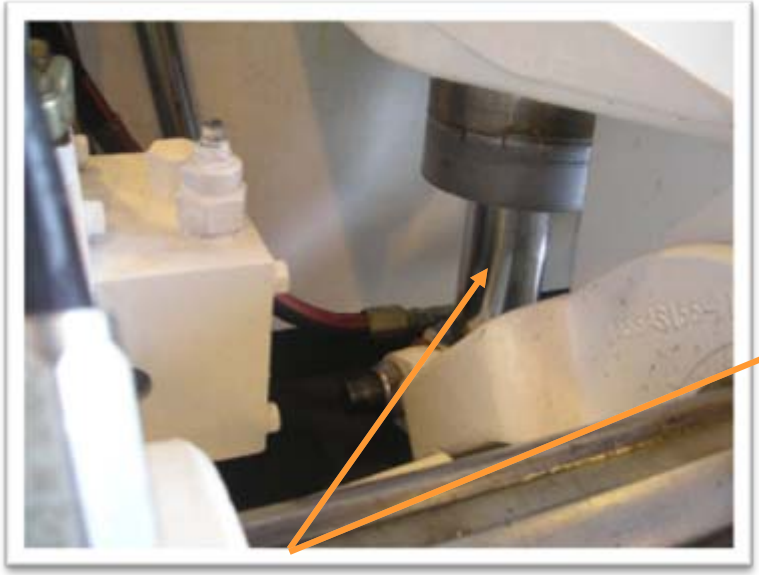
Official part identification pending

Proposed Demo Components

SERDP PP-1152 | ESTCP WP-0411 | Supplemental | ESTCP WP-0936

NAVAIR Lakehurst – Ground Support Equipment

- **Telescoping Hydraulic Cylinder (Spotting Dolly)**



Telescoping Hydraulic Cylinder

Spotting Dolly

Proposed Demo Components

SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

NAVSEA (NESDI & OSD Leveraged Effort)

- **Marine Corps MK48 LVS (Logistic Vehicle System) Hydraulic Cylinders**
  - Evaluate coatings in accelerated corrosion cabinet (GM9540P) and marine atmospheric test exposures
  - Field test optimum coating systems on MK48 vehicles
  - Develop selection criteria for implementation into system repair / rebuild and spare parts sourcing
  - Reduce corrosion maintenance requirements and repair costs of vehicles

Summary

- **Nanocrystalline Co-P Process (a.k.a. Nanovate™ CR)**
  - Environmentally compliant EHC alternative
  - Process compatible with existing plating infrastructure
  - Reduced energy consumption, increased throughput
- **Nanocrystalline Co-P Properties**
  - Enhanced corrosion and wear
  - Non-embrittling
  - Improved fatigue performance vs. EHC
- **Future work (WP-0936)**
  - Performance testing (JTP)
  - Dem/val at NAVAIR JAX Depot

For more information…

INTEGRAN TECHNOLOGIES INC.

Visit our booth at ASETS Defense

Diana Facchini, MASc
Project Leader
Integran Technologies, Inc.
416-675-6266 x 236
facchini@integran.com

Ruben Prado, CEF
Principal Investigator
Naval Air Systems Command
904-542-3444 x 106
Ruben.prado@navy.mil

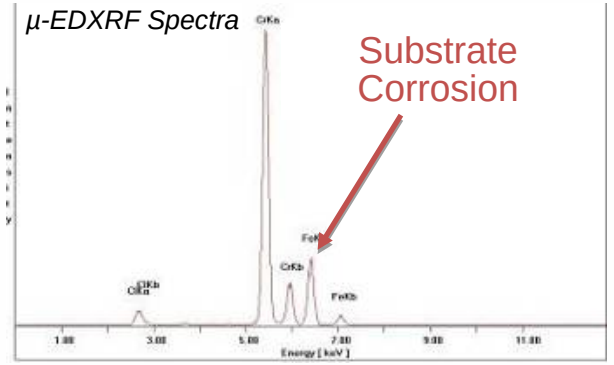
Backup Slides

Data Acquisition
(Corrosion)

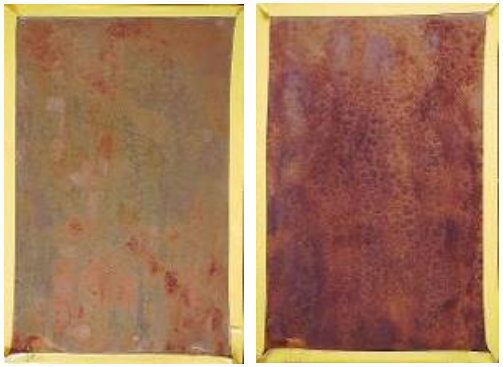
SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

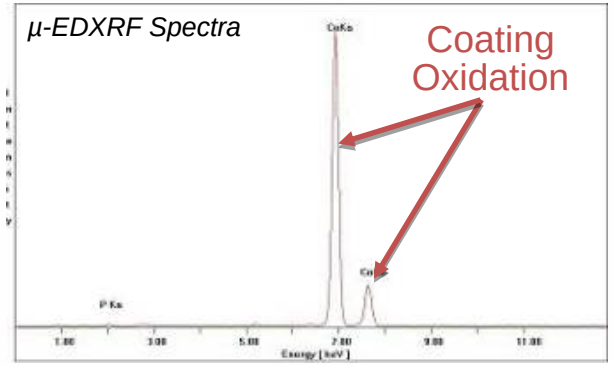
- **Testing with downselected plating conditions**
- ASTM B117 Salt Fog
  - 165 h exposure
- EHC exhibits red rust
- nCoP exhibits coating oxidation
  - No red rust

Hard Chrome



nCoP

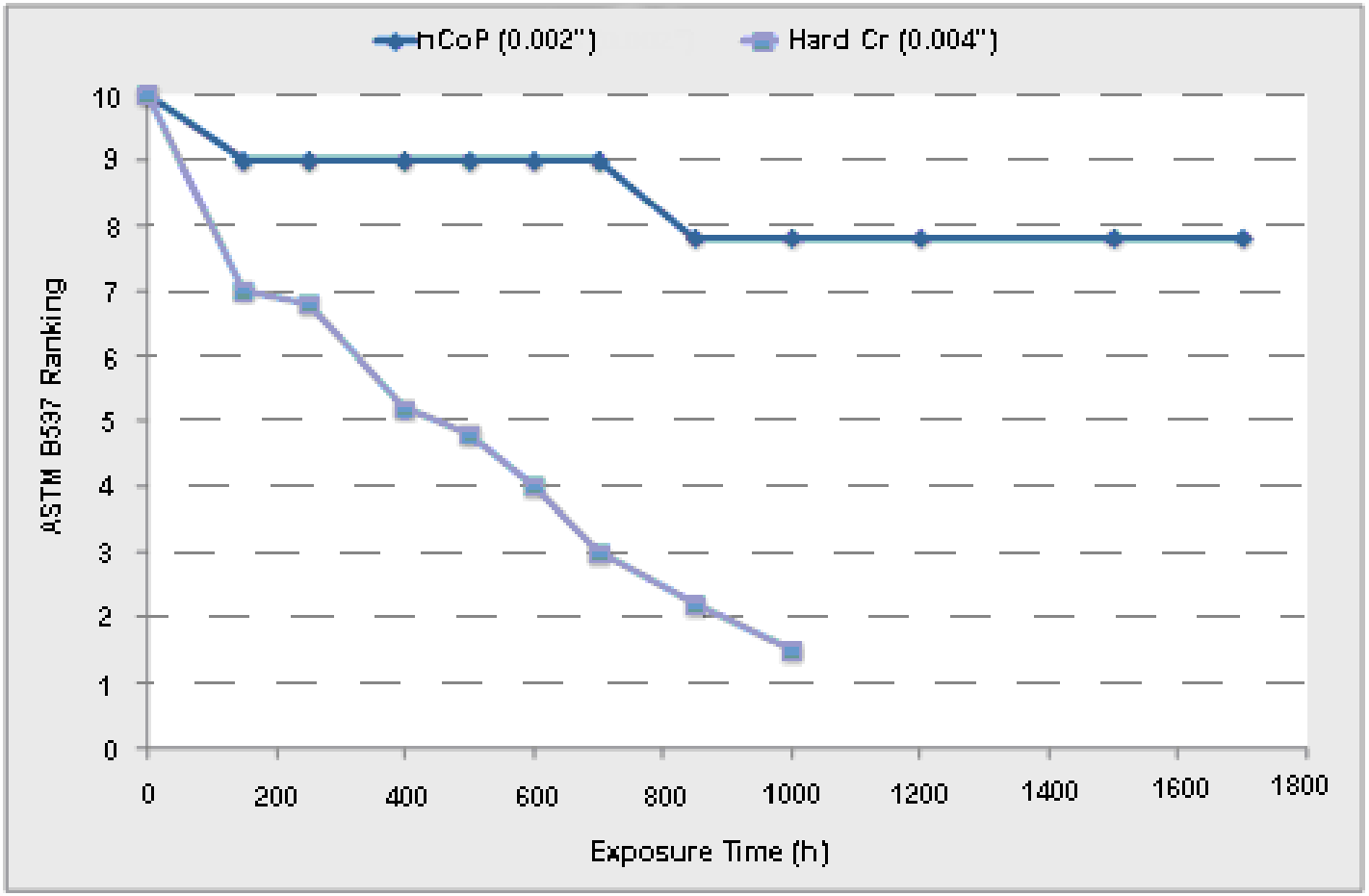




Corrosion Testing

SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

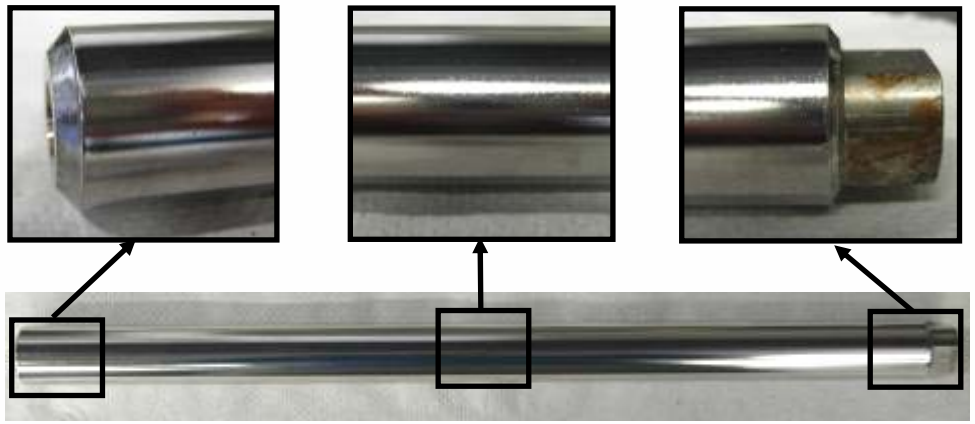
- ASTM B117 Salt Spray, 1000 hrs exposure



Rod-Seal Wear Testing

SERDP PP-1152 → ESTCP WP-0411 → Supplemental → ESTCP WP-0936

- Four PH 13-8Mo hydraulic actuator rods
  - Plated with 0.006-0.008” nCoP
  - Hydrogen baked (375°F, 23h) or heat treated (300°C, 6 h)
  - Ground to 6-9 µinch, 12-16 µinch or superfinished to Ra < 4 µinch
- Testing conducted at NAVAIR-PAX
  - similar to ID cylinder wear - wear against seals
  - Tests showed nCoP comparable to Cr

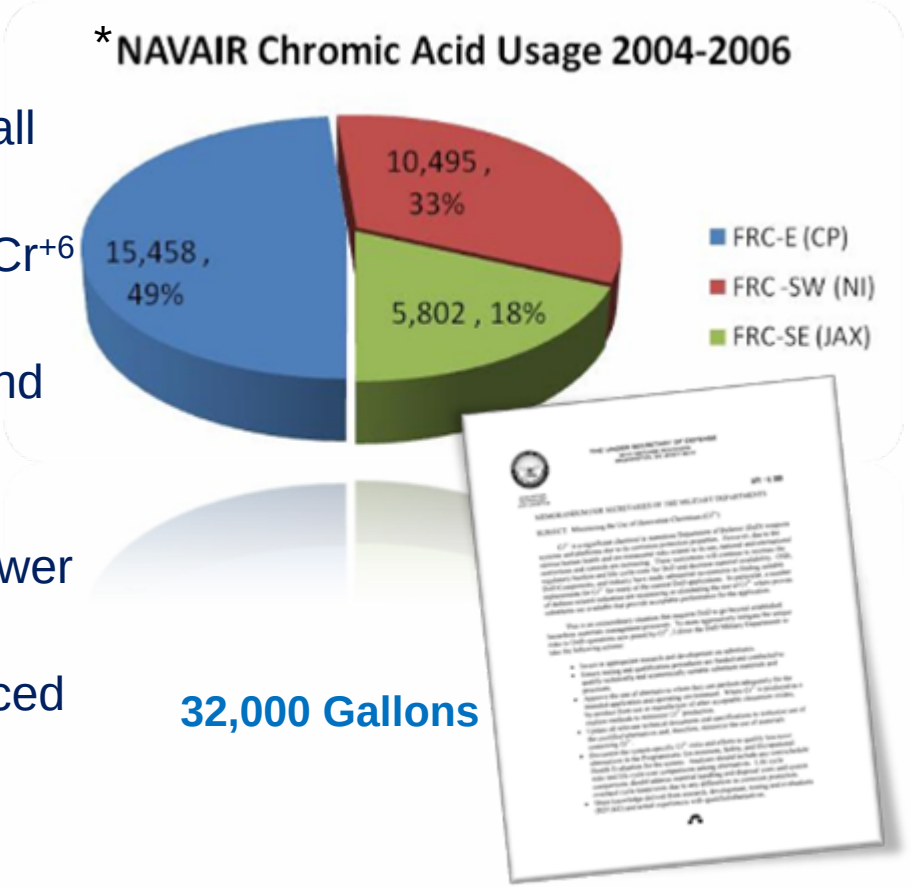


nCoP-coated hydraulic rod

Rod-seal test apparatus

Environmental Driver/Benefit

- **Environmental Benefits**
  - Eliminates chrome plating and all its hazardous waste
  - Eliminates worker exposure to Cr^{+6}
  - Primary cost savings from reduced engineering controls and all required maintenance/monitoring
  - Some savings from reduced power use (more efficient process)
  - Increased throughput and reduced footprint through reduction of process tanks

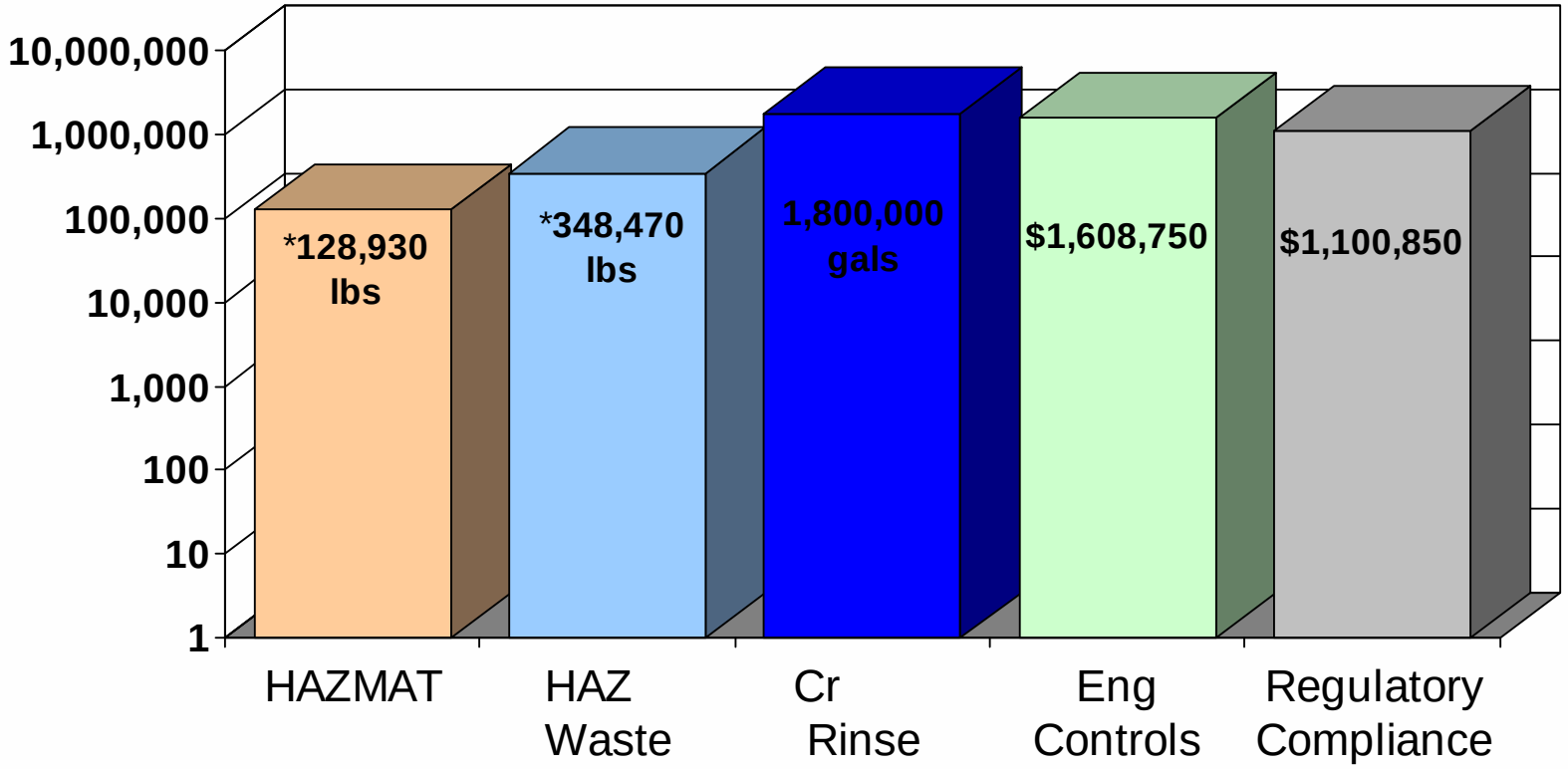


** Data obtained from NAVAIR's Environmental Systems Allocation (ESA) Model. Extend to: Actuators, Landing Gear, Gear and engine journals and wear surfaces on Aircraft, Vehicles & Vessels*

Environmental Driver/Benefit

(Hexavalent Chromium Plating at Navy FRCs)

- **Estimated NAVAIR P2 Savings over 10 Yrs**



Note: the above projected savings are assumptions based on FRC-SE data extrapolated to other Navy FRCs

** Estimated amounts due to chrome plating based on average Environmental Systems Allocation (ESA) data extrapolated across all FRCs over a 10 yr period*

IH Assessment at NAVAIR JAX

- NAVAIR-JAX IH assessment on Co emission on the Dem/Val tank.

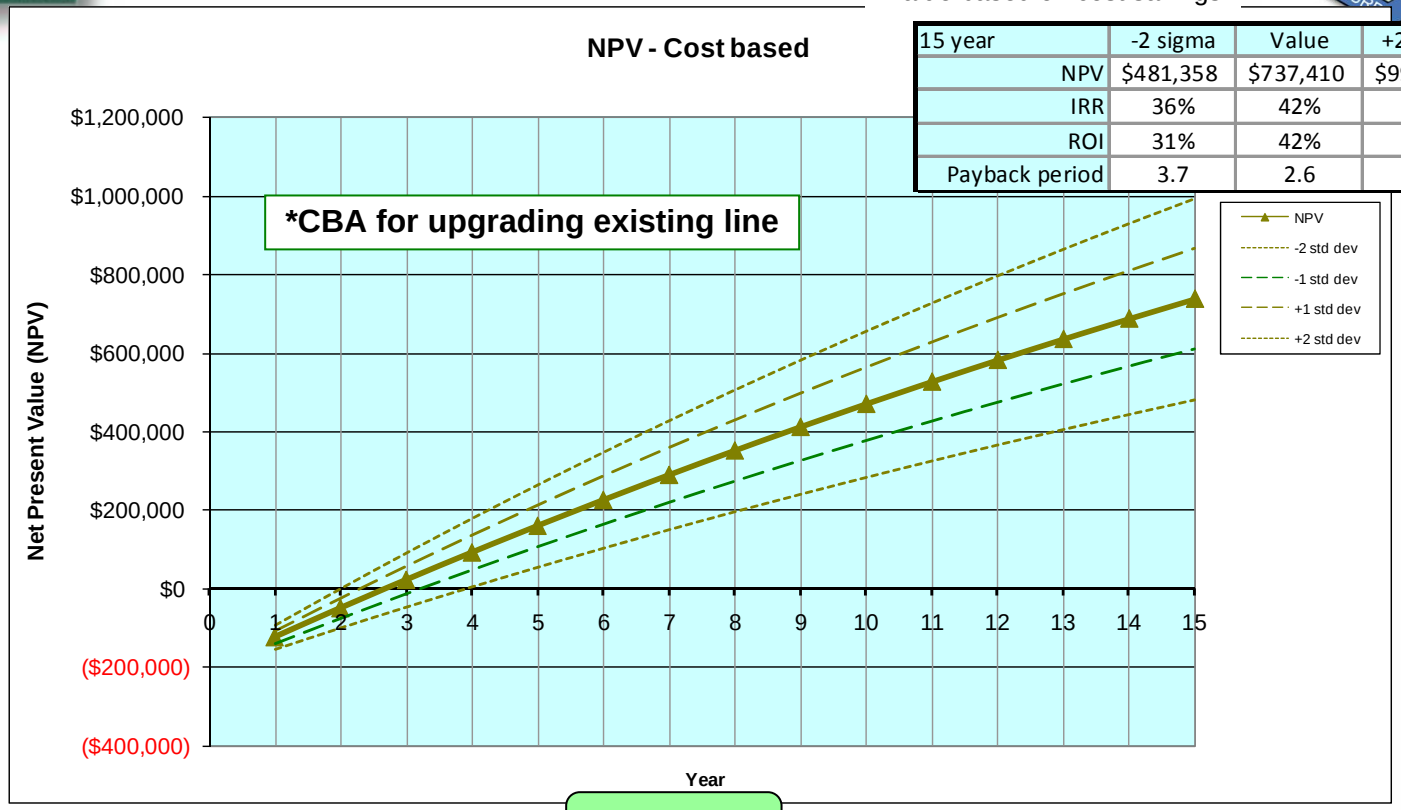
DATE:	PERSONAL SAMPLING RESULTS (8-HR TWAS)	AREA SAMPLING RESULTS (8-HR TWAS)	VENTILATION MEASUREMENTS (TAKEN ON THE PULL SIDE)	DRY BULB READINGS (2)	RELATIVE HUMIDITY (3)
8 Aug 2007	Below the LOD	0.0023 mg/m^3	3519 FPM	Initial: 79.1^{o}F Final: 97.3^{o}F	Initial: 100% Final: 58%
9 Aug 2007	Below the LOD	0.0074 mg/m^3	3545 FPM	Initial: 81.2^{o}F Final: 97.6^{o}F	Initial: 100% Final: 58%
16 Aug 2007	Below the LOD	0.0017 mg/m^3	4001 FPM	Initial: 79.0^{o}F Final: 94.4^{o}F	Initial: 91% Final: 51%
22 Aug 2007	Below the LOD	Below the LOD	4366 FPM	Initial: 78.5^{o}F Final: 95.0^{o}F	Initial: 94% Final: 50%
24 Aug 2007	Below the LOD	Below the LOD	4088 FPM	Initial: 77.5^{o}F Final: 94.2^{o}F	Initial: 100% Final: 58%

Co PEL is 20 µg/m^3

Cost Benefit Analysis

Value based on cost savings

15 year	-2 sigma	Value	+2 sigma
NPV	$481,358	$737,410	$993,463
IRR	36%	42%	47%
ROI	31%	42%	53%
Payback period	3.7	2.6	2.0



*ROI: 42% w/ Payback Period of **2.6 yrs**

	EHC	nCo-P
Labor	$1,365	$1,365
Chemicals	$1,503	$1,585
Water	$6	$62
Electricity	$24	$1

Average cost/item

- Same labor
- More expensive chemicals
- Higher bath temperature
- Faster, more efficient plating